THERMAL AGEING OF VINYLESTER NEUTRON SHIELDING USED IN TRANSPORT/STORAGE CASKS

F. NIZEYIMANA
TN International (AREVA group) BP 302, F-78054 Saint Quentin en Yvelines

V. BELLENGER
Arts & Métiers ParisTech, 151 Bd Hôpital, F-75013 Paris

P. ABADIE †
TN International (AREVA group) BP 302, F-78054 Saint Quentin en Yvelines

H. ISSARD
TN International (AREVA group) BP 302, F-78054 Saint Quentin en Yvelines

ABSTRACT

A mineral filled vinylester composite used in radioactive materials transport/storage casks as a neutron shielding has been studied. The matrix is a highly hydrogenated novolac-type vinylester resin and two mineral fillers are zinc borate and aluminium tri hydrate. During the use of casks, neutrons are slowed down by hydrogen atoms contained in both resin and fillers, and then absorbed mainly by boron atoms contained in zinc borate. Aluminium tri hydrate is used for the material fire resistance and self-extinction properties. During the service life of the transport/storage casks, the neutron shielding material is subjected to three types of ageing: thermal degradation, irradiation and hydrolysis. In this paper, only thermal ageing results are discussed.

The composite was cast under room temperature, cured at 80°C for 12 hours, and then post-cured at 160°C for 4 hours before ageing experiments. Gravimetric analysis data were used to evaluate weight loss of the composite after exposure to various temperatures ranging from 120°C to 160°C, under atmospheric pressure and 2×10^5 Pa of oxygen pressure. During the first hours of ageing, a fast weight loss was observed due to volatility of low molecular weight compounds. Then, over ageing time, the rate of weight loss decreased. Fourier transform infrared (FTIR) spectroscopy measurements were carried out in transmission mode to investigate C-H aliphatic bonds consumption and carbonyl functions build up. In addition, glass temperature (Tg) was monitored using dynamic mechanical thermal analysis (DMTA). To investigate the effect of thermal ageing on the composite mechanical properties, flexural modulus and ultimate stress were determined prior and after exposure.

Key words: ageing, neutron shielding, vinylester, mineral fillers, gravimetric analysis, FTIR, DMTA, flexural modulus and ultimate stress.

1. INTRODUCTION

In recent years, vinylester (VE) polymer composite materials are widely used in various applications, such as offshore industry and civil engineering industry. For this reason, in literature, most of studies deal with the hydrolytic degradation of vinylester materials [1-3]. Moreover, the few authors who worked on thermal and thermo-oxidative ageing of VE materials applied Arrhenius relationship-based models to predict their long-term behavior [4-6].

However, these models are empirical and very controversial [7,8]. Basically, a chemical process is assumed to be accelerated exponentially with the increase of temperature [9]. Materials are submitted to accelerated tests (with various temperatures) in isotherm conditions. Then, durations needed to reach the critical degradation state are measured and extrapolated to service temperature. In this regard, an important point must be taken into account: a degradation mechanism must be predominant and exposure to high temperatures should not alter degradation path observed under service conditions [10].

More recently, an advanced thermo-oxidative model has been applied to predict long-term behavior of epoxy composites [11], where oxidation kinetic scheme established by Bolland and Gee [12] is coupled with the equation of oxygen diffusion. The aim of our study is using this methodology in order to predict the long term behavior of a mineral-filled vinylester composite (TN Vyal B^{TM}). Since the neutron shielding capacity of this polymer composite material relies on hydrogen atoms which slow down neutrons, it is essential to study hydrogen atom concentration at long term and overall weight loss of samples. During ageing, hydrogen consumption is followed by carbonyl groups build-up. To investigate these chemical changes, Fourier Transform Infrared (FTIR) spectrometry has been used.

Although Vinylester materials are known to display a good thermal and mechanical stability, changes of all these properties may occur under specific service conditions. In this study, glass transition temperatures are measured using Dynamic Mechanical Thermal Analysis (DMTA), while mechanical properties are assessed by measuring flexural modulus and ultimate stress.

2. MATERIAL AND EXPERIMENTAL METHODS

2.1 Material

The material studied is composed of a novolac-type vinylester matrix containing 36 wt% of styrene as a solvent, and two mineral fillers: aluminum tri hydrate (ATH) and zinc borate (ZB). The mixture of matrix (32%) and fillers (68%) was cast at ambient temperature, cured at 80°C for 12 hours and post-cured at 160°C for 4 hours.

2.2. Experimental methods

Gravimetric analysis

Composite samples were cut to a size of 25*0.5mm, 25*0.7mm and 25*0.4mm. Then, these cylindrical samples were weighed out using a Mettler Toledo balance with a relative accuracy of 10^{-4} and exposed to various temperatures ranging from 120°C to 160°C and oxygen pressure (atmospheric pressure and 2×10^{5} Pa). Weight variations (%) of aged samples were periodically determined as follows:

$$\frac{\Delta m}{m_0}\ (\%) = \frac{m_t - m_0}{m_0} \times 100 \qquad (1)$$

Where m_0, m_t are initial weight and weight at ageing time t, respectively.

Numerical modeling of gravimetric results was obtained by applying the same methodology used in our laboratory for several years so far. This approach of ageing model is based on a mechanistic scheme and a set of differential equations. It is widely detailed elsewhere [11]. To solve the differential equations system, Matlab software is needed.

Except ageing at 160°C and 2×10^5Pa where simulation showed excellent fitting with experimental data of weight loss, for other ageing conditions, only experimental results will be discussed. Simulation calculations are under further investigation and are likely to be completed in 2011.
The main parameters used for Matlab resolution are listed in table 1.

Table 1. Matlab parameters used for modeling weight loss of samples exposed to 160°C, 2×10^5 Pa

$[PH]_0$ mol/l	$[POOH]_0$ mol/l	$Dens_0$ kg/m^3	Volat	Cs mol/l	Cte_1 l mol^{-1} s^{-1}	Cte_2 l mol^{-1} s^{-1}	2β mol/l	Ψ 0.1	Ro l mol^{-1} s^{-1}
40	10^{-4}	$1.18\ 10^3$	69	$39.5 10^{-3}$	10^{-1}	10^8	172	0.1	6.4×10^{-6}

- $Cte_1 = k_1$ • $Cte_2 = k_2$ • $Cte_3 = k_3 \times [PH]_0$ • $2\beta = \dfrac{k_2 \times k_6}{k_3 \times k_5 \times [PH]_0}$ • $\Psi = 4 \times \dfrac{k_4 \times k_6}{k_5^2}$

$$Ro = \dfrac{k_3^2 \times [PH]_0^2}{k_6}$$

- The diffusivity (D) value used here (8×10^{-12}m^2/s), was calculated from the value measured at room temperature and the activation energy, E_a equal to 19 kJ/mol.

Dynamic Mechanical Thermal Analysis

Dynamic mechanical thermal analysis tests were carried out on 20*5*2mm samples using a NETZCH DMA 242 intrument in a tensile mode. Tests were run at a temperature range of 30-200°C with a heating rate of 5°C/min and a frequency of 1Hz. Glass temperature of the unaged composite was determined: 130°C.

FTIR Spectroscopy

IR spectra were recorded using a Fourier transform infrared Brucker IFS 28 spectrometer in transmission mode in the 4000-400 cm^{-1} region. Beer-Lambert law was applied to monitor the carbonyl group build-up as a function of ageing time.
Absorbance values of carbonyl group (1727 cm^{-1}) were quantified by rationing them to the aromatic C=C stretching absorbance (1494 cm^{-1}). This aromatic peak considered as an internal reference remained stable during ageing.

Mechanical analysis

Mechanical tests were carried out on Instron 5880 in three-point bending mode in accordance with a French standard NF T51-001. Flexural moduli and ultimate stresses were determined and plotted versus ageing time and temperature.

3. RESULTS AND DISCUSSION

3.1. Gravimetric analysis

To determine the effect of oxygen (O_2) pressure, VE composite samples were aged at 160°C with two various O_2 pressure: atmospheric pressure and 2×10^5 Pa. Figure 1 shows higher weight loss rates during the first 48 hours followed by smaller but progressive weight loss rates. The first phase corresponds to extraction (volatility) of low molecular weight species and unreacted molecules (accelerator, styrene...) and the beginning of oxidation reactions. The second phase of weight loss is only due to thermo-oxidative process. Overall mass loss % increased with surface/volume (S/V) ratio and oxygen pressure; for instance, considering samples of 25*0.5mm, mass loss % was 3.6 at atmospheric pressure and 5.5 at 2×10^5 Pa.

The weight loss simulated curve of 25*0.7mm samples exposed to 2×10^5 Pa is shown in fig 3. Simulated data are consistent with experimental results; hence, the experimental weight loss values are corrected taking into account the volatility of low molecular species and unreacted molecules (1.34%).

The influence of temperature was studied by comparing weight losses at 120°C and 140°C with the same oxygen pressure (2×10^5 Pa). A little difference was observed; the first phase of extraction took more than 48 hours at both temperatures (250h and 1200h at 140°C and 120°C respectively). Then, a second phase appears, where mass loss rate is very slow, they are even positive at 120°C. This phenomenon is due to competition between weight gain (O_2 grafting to the material) induced by propagation reactions and weight loss induced by termination reactions. When the length of radical chains of oxidation becomes shorter, weight loss becomes predominant which corresponds to the third. It is also important to point out that overall weight loss at 120°C is far slower comparing to other temperatures, for instance, it is roughly equal to 0.8% at 120°C and 3.5% at 140°C.

(a)   (b)
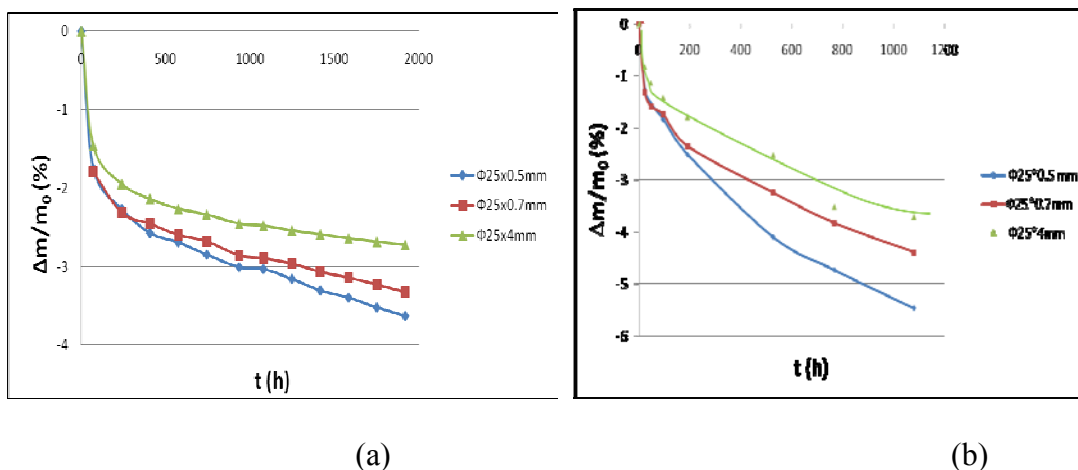
Figure 1. The evolution of mass loss with ageing time, samples thicknesses and O_2 pressure: (a) atmospheric pressure, (b) Oxygen $_{pressure}$ = 2×10^5 Pa, at 160°C.
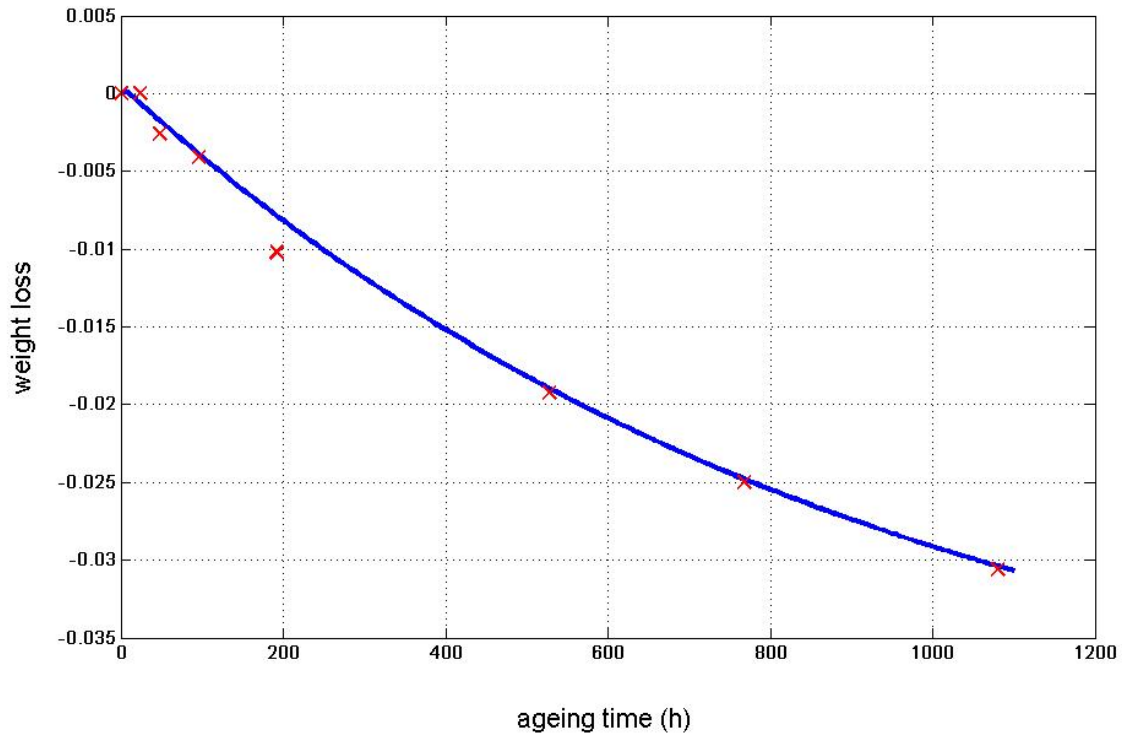
Figure 2. Experimental (×) and calculated (-) weight loss of 25*0.7 mm samples. 160°C, 2×10^5 Pa


(a)

(b)
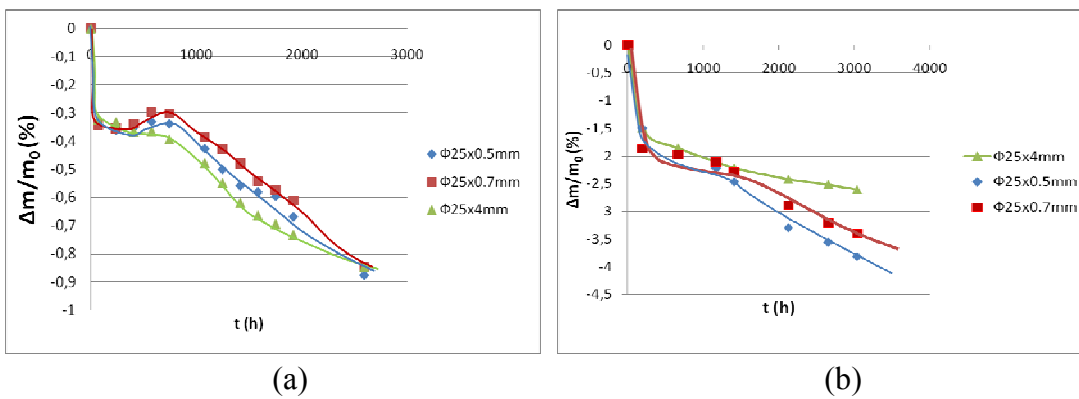
Figure 3.The evolution of mass loss with ageing time, temperature and samples thicknesses: (a) 120°C; (b) 140°C. Oxygen $_{pressure}$ = 2×10^5 Pa.

3.1. FTIR SPECTROSCOPY

Figure 4 shows the evolution of the ratio of carbonyl groups absorbance and internal reference as a function of ageing time, temperature and oxygen pressure. Two observations can be pointed out:

• Oxygen pressure accelerates considerably carbonyl groups build-up; in fact at 140°C and 160°C with O_2 pressure of 2×10^5 Pa, carbonyl groups concentrations are higher than concentrations values obtained at 160°C under atmospheric pressure.

• Carbonyl groups build-up increased with temperature, but at the glassy state (120°C), it increased very slowly.
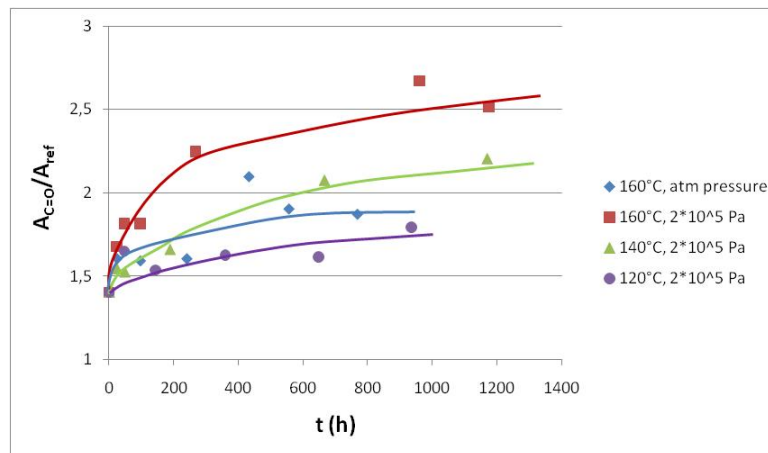
Figure 4. The evolution of absorbance (A/A_{ref}) of carbonyl groups during exposure to various temperature and O_2 pressure.

3.3. MECHANICAL PROPERTIES

Mechanical properties are studied because they are a very sensitive indicator of chemical structure degradation induced by ageing. Flexural moduli and ultimate stresses of unaged composite are equal to 10500 ± 1325 MPa and 65 ± 7 MPa respectively. The high value of flexural modulus is comparable to the value of 10 300 MPa obtained by Fraga et al. [3] on a vinylester/verre composite. The evolution of Flexural moduli and ultimate stresses values plotted against ageing time are shown in figure 5. No significant changes of E and σ_R were observed. Therefore, from a mechanical point of view, the thermal stability of our material is confirmed. However, mechanical properties results are somewhat surprising when considering the behavior in DMTA. In fact, glass temperature (Tg) values increased continuously with ageing time until 600 hours. Tg values increased from 130°C for virgin composite to about 165°C for aged samples at all studied environments. The increase of Tg is due to variation of the chemical structure and/or the chemical composition of TN Vyal B[TM], but this variation has no effect on the mechanical behavior.
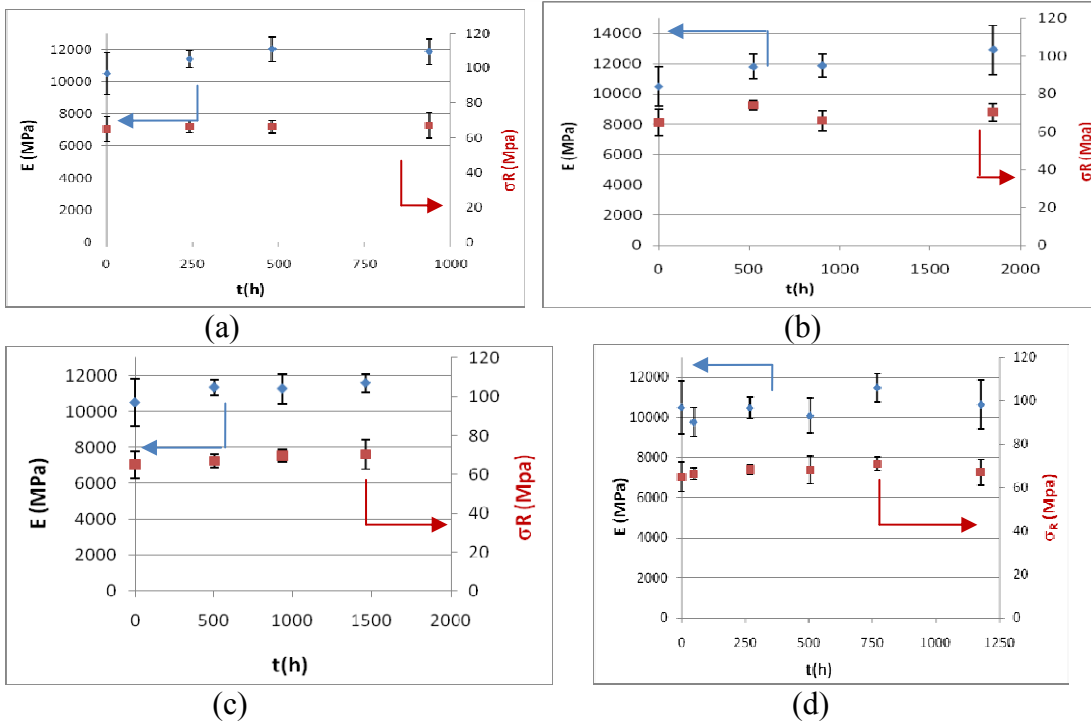
Figure 4. Flexural moduli and ultimate stresses of vinylester composite after exposure to (a) 120°C, 2×10⁵ Pa, (b) 140°C, 2×10⁵ Pa, (c) 160°C, atmospheric pressure and (d) 160°C, 2×10⁵ Pa

CONCLUSIONS

Gravimetric analysis showed that thermo-oxidative ageing of this neutron shielding Vinylester composite depends on oxygen pressure, temperature and samples S/V ratio. It was observed that the oxygen pressure and temperature were associated to accelerate samples weight losses. Mechanical properties stability was assessed by measuring both flexural moduli and ultimate stress of aged samples. The next step of our study will focus on numerical modeling of overall weight losses, hydrogen atoms depletion with ageing time as well as oxidation products present on superficial oxidative layer.

REFERENCES

1. Ghorbel I., Valentin D., *Hydrothermal effects on the physico-chemical properties of pure and glass fiber reinforced polyester and vinylester resins*, Polymer composites, 1993. 14: p. 324-334.

2. Ganem M., Mortaigne B., Bellenger V. & Verdu J., *Hydrolytic ageing of vinylester materials, part1: ageing of prepolymers and model compound*, polym. Network blends, (1994) 4, 87-92

3. Fraga A.N., Alvarez V.A., Vasquez A., *Relationship between dynamic mechanical properties and water absorption of unsaturated polyester and vinylester glass fiber composites*. Journal of Composite Materials, 2003. **37**(17): p. 1553-1574.

4. Issard H., *2nd ASTM Seminar on accelerated testing of materials in spent neclear fuel and high lever waste storage systems*. Tampa, Florida, January 31-February 1, 2008.

5. Yokoe D., Taniuchi H., Akamatsu H., Shimoyo J., Abadie P., *Proceedings of the 15th int. symp. on packaging and transportation of radioactive materials*. Miami, october 2007

6. Abadie P., *14th int. symp. on the packaging and transportation of radioactive materials*. PATRAM 2004, September 20-24, 2004 (Berlin, Germany)

7. K.T. Gillen, M. Celina, R. Clough and J. Wise, *Extrapolation of accelerated aging data-Arrhenius or Erroneous?* TRIP, 1997, 5 (8) 250-257

8. Celina M., Gillen K.T. and Assink R.A., *Accelerated aging and lifetime prediction : review of non Arrhenius behavior due to two competing processes*, Polym Deg Stab , 2005, 90, 395-404

9. Nelson W., Accelerated testing: statistical models, test plans and data analyses. New York, John Wiley and sons, 1990.

10. Bank, L.C., T.R. Gentry, B.P. Thomson, J.S. Russel, *A model specification for FRP composites for civil engineering structures*. Construction and Building Materials, 2003. **17**(6-7): p. 405-437.

11. Decelle J., Huet N., Bellenger V., *Oxidation induced shrinkage for thermally aged epoxy networks*, Polymer degradation stability 81 (2003) 239-248

12. Bolland J.L., Gee G., *Kinetic studies in the chemistry of rubber and related materials*, Trans. Faraday Soc. 42: p. 236-243 (1946)